

## DETAILED ACTION

### *Continued Examination Under 37 CFR 1.114*

1. A request for continued examination under 37 CFR 1.114, including the fee set forth in 37 CFR 1.17(e), was filed in this application after final rejection. Since this application is eligible for continued examination under 37 CFR 1.114, and the fee set forth in 37 CFR 1.17(e) has been timely paid, the finality of the previous Office action has been withdrawn pursuant to 37 CFR 1.114. Applicant's submission filed on September 16, 2008 has been entered.

The amendment filed with the RCE submission of September 16, 2008 has been received and entered. With the entry of the amendment, claim 15 has been canceled, and claims 1-14, 16-17, and new claims 18-21 are pending for examination.

### *Claim Rejections - 35 USC § 112*

2. The following is a quotation of the second paragraph of 35 U.S.C. 112:

The specification shall conclude with one or more claims particularly pointing out and distinctly claiming the subject matter which the applicant regards as his invention.

3. Claims 14 and 17 are rejected under 35 U.S.C. 112, second paragraph, as being indefinite for failing to particularly point out and distinctly claim the subject matter which applicant regards as the invention.

Claim 14, lines 2-3, refers to "the native oxide" thickness. However, a "native" oxide is not referred to in claim 1, so this lacks antecedent basis. For the purpose of

examination, the Examiner has considered to term to simply mean "the oxide" thickness.

Claim 17, lines 3, refers to "the native oxide" thickness. However, a "native" oxide is not referred to in claim 8, so this lacks antecedent basis. For the purpose of examination, the Examiner has considered to term to simply mean "the oxide" thickness.

#### *Claim Rejections - 35 USC § 103*

4. The following is a quotation of 35 U.S.C. 103(a) which forms the basis for all obviousness rejections set forth in this Office action:

(a) A patent may not be obtained though the invention is not identically disclosed or described as set forth in section 102 of this title, if the differences between the subject matter sought to be patented and the prior art are such that the subject matter as a whole would have been obvious at the time the invention was made to a person having ordinary skill in the art to which said subject matter pertains. Patentability shall not be negated by the manner in which the invention was made.

5. This application currently names joint inventors. In considering patentability of the claims under 35 U.S.C. 103(a), the examiner presumes that the subject matter of the various claims was commonly owned at the time any inventions covered therein were made absent any evidence to the contrary. Applicant is advised of the obligation under 37 CFR 1.56 to point out the inventor and invention dates of each claim that was not commonly owned at the time a later invention was made in order for the examiner to consider the applicability of 35 U.S.C. 103(c) and potential 35 U.S.C. 102(e), (f) or (g) prior art under 35 U.S.C. 103(a).

6. Claims 1, 2, 4, 7-9, 13, 14 and 16-21 are rejected under 35 U.S.C. 103(a) as being unpatentable over the admitted state of the prior art in view of Kawanoue et al (US 6229211).

The admitted state of the prior art, at pages 1-4 of the specification, teaches a known process for making embedded multilevel interconnects. For example, the process includes forming a hole portion in an insulating layer (page 2, line 25 through page 3, line 7). Then a barrier metal film of TaN is formed on the hole portion walls, by a method such as sputtering (page 3, lines 5-10). The applied barrier metal film of TaN is exposed to the atmosphere to form an oxide film (page 3, lines 8-11). The oxide film formed on a surface of the barrier metal film is removed by etching (page 3, lines 5-15). Then, an electroless plating step of immersing the barrier metal film in a plating liquid comprising copper, thereby forming an electroless copper plating film on the barrier metal film occurs (page 3, lines 15-18).

Claims 7, 13: Finally, an electrolytic copper plating step occurs over the electroless copper plating film (which thereby acts as the seed layer for the electrolytic plating) (page 3, lines 18-21).

The admitted state of the prior art teaches all the features of these claims except (1) the element composition ratio of N/Ta (claims 1, 2, 8, 9, 18-21), (2) the removal step is such that the barrier metal film is left in such a manner that it entirely covers the inner wall of the hole portion (claim 4), (3) by controlling the composition and thickness of the barrier metal film, after the removal step the barrier metal film is left in such a

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manner that it essentially entirely covers the inner wall of the hole portion (claim 8), (4) controlling the element composition ratio to provide native oxide thickness less than 1 nm/0.5 nm (claims 1, 8, 14, 16-17).

However, Kawanoue teaches barrier metal films that can be used when forming embedded multilevel interconnection, where a copper layer is applied over the barrier films. Column 1, lines 5-40, column 8, lines 5-25 and Figures 3B and 3D, for example. A barrier film is applied to a hole portion area of an insulating layer. Figures 3B and 3D, for example, and column 8, lines 5-25. The barrier film can be tantalum nitride, and can be formed by sputtering. Column 3, lines 50-65 and column 8, lines 5-25 and 50-65. The ratio of nitrogen to tantalum (N/Ta) can be 1.19, for example. Figures 3A and 3E, for example, and column 8, lines 1-30 (film 32 or film 39). The ratio of nitrogen to tantalum (N/Ta) can also be 0.87, for example. Figures 3B and 3D, for example, and column 8, lines 5-25. Therefore, when depositing, the composition of the barrier metal film is controlled (see column 7, lines 55-60). Kawanoue further teaches that the composition ratio of a TaN layer can be such that N/Ta is  $>1$  ( $\text{TaN}_x$ ,  $x > 1$ ) (with  $x$  being other than 1.19, for example) as long as alternate layers of  $\text{TaN}_y$ ,  $y \leq 1$ , are also used. Column 10, lines 30-45. As well, Kawanoue describes the use of a TaN barrier layer with a ratio of nitrogen to tantalum (N/Ta) of 1.4. Column 22, lines 30-35 and figure 30. The thickness of the applied barrier metal film is also controlled. See column 7, lines 45-55 (20 nm on the bottom and 5 nm on the side walls). When copper is applied over the barrier film,

the barrier film is provided in such a manner that it entirely covers the inner wall of the hole portion. Figures 3A and 3E and column 7, lines 45-55.

It would have been obvious to one of ordinary skill in the art at the time the invention was made to modify the admitted state of the prior art to use a N/Ta ratio of 0.87 or 1.19, for example, and control the composition of the barrier metal film applied to provide this ratio, as suggested by Kawanoue with an expectation of desirable protective barrier action, because the admitted state of the prior art teaches the desire to provide TaN films by a method such as sputtering for forming barrier films for embedded multilevel interconnects, and Kawanoue teaches that TaN films provided by a method such as sputtering for forming barrier films for embedded multilevel interconnects can acceptably have a N/Ta ratio of 1.19, beneficially when used with other layers of TaN with an N/Ta ratio of  $\leq 1$  or a N/Ta ratio of 0.87, beneficially when used with other layers of TaN with an N/Ta ratio of  $>1$ . Furthermore, as to claims 19 and 21 (N/Ta ratio of  $1.3 < \text{N/Ta} < 1.5$ ), the Examiner notes that Kawanoue provides the use of a barrier layer of N/Ta of 1.4, for example. Furthermore, it would also have been obvious to modify the admitted state of the prior art to perform the removal step such that the barrier metal film is left in such a manner that it entirely covers the inner wall of the hole portion when copper coating is performed as suggested by Kawanoue in order to provide a desirable copper plating, because the admitted state of the prior art provides applying a barrier film to hole walls and etching the barrier film (to remove oxide) prior to applying copper and Kawanoue teaches that it is well known when

applying a barrier film to hole walls prior to applying copper, to have the barrier film covering all of the hole walls before applying the copper. Furthermore, it would also have been obvious to modify the admitted state of the prior art to control the thickness of the barrier metal film when applying as suggested by Kawanoue to provide predictable repeatable results, because the admitted state of the prior art teaches the desire to provide TaN films by a method such as sputtering for forming barrier films for embedded multilevel interconnects, and Kawanoue teaches that TaN films provided by a method such as sputtering for forming barrier films for embedded multilevel interconnects are desirably applied to a controlled thickness such as 20 nm on the bottom and 5 nm on the side walls, and further shows that this thickness covers all the hole walls before applying the copper, and one of ordinary skill in the art would wish to apply coatings to a controlled repeatable thickness for repeatable results. As to the claimed "by controlling the composition and the thickness of the barrier metal film, after removal of the oxide film the barrier metal film essentially entirely covers the inner wall of the hole portion, thereby preventing development of a void within the hole portion" (claim 8), the fact that applicant has recognized another advantage which would flow naturally from following the suggestion of the prior art cannot be the basis for patentability when the differences would otherwise be obvious. See *Ex parte Obiaya*, 227 USPQ 58, 60 (Bd. Pat. App. & Inter. 1985). Here, the admitted state of the prior art in view of Kawanoue provides applying the barrier metal film within the composition range claimed and a thickness greater than that required by applicant for essentially

entirely covering the inner wall to prevent developments of void, and therefore the claimed "after removal of the oxide film the barrier metal film essentially entirely covers the inner wall of the hole portion, thereby preventing development of a void within the hole portion" occurs. As to the claimed choosing the N/Ta ratio to control film thickness of the native oxide to be 1 nm/0.5nm or thinner (claims 1, 8, 14, 16, 17), the fact that applicant has recognized another advantage which would flow naturally from following the suggestion of the prior art cannot be the basis for patentability when the differences would otherwise be obvious. See *Ex parte Obiaya*, 227 USPQ 58, 60 (Bd. Pat. App. & Inter. 1985). Here, the admitted state of the prior art in view of Kawanoue provides choosing and applying the barrier metal film within the ratio claimed (0.87, 1.19, 1.4, for example) for claims 1, 2, 8, 9, and 18-21, and therefore the claimed native oxide thickness of 1 nm/ 0.5mm or thinner will occur (as shown by applicant's Figure 2 and specification at page 9).

7. Claims 3 and 10 are rejected under 35 U.S.C. 103(a) as being unpatentable over the admitted state of the prior art in view of Kawanoue as applied to claims 1, 2, 4, 7-9, 13, 14 and 16-21 above, and further in view of Miyamoto (US 6284649).

The admitted state of the prior art in view of Kawanoue teaches all the features of these claims except that the TaN film is formed by plasma nitriding tantalum.

However, Miyamoto teaches a method of forming a tantalum nitride barrier layer to use in semiconductor devices, where the barrier layer is applied in a connection

hole and then Cu is applied over the barrier layer. Column 1, line 35 through column 2, line 10. Miyamoto teaches that one way to achieve the tantalum nitride barrier layer is to apply a tantalum layer and then performing plasma nitriding to form the tantalum nitride. Column 10, lines 1-55 and column 9, lines 1-30.

It would have been obvious to one of ordinary skill in the art at the time the invention was made to modify the admitted state of the prior art in view of Kawanoue to achieve the tantalum nitride barrier film by applying tantalum and plasma nitriding as suggested by Miyamoto in order to provide a desirable barrier film, because the admitted state of the prior art in view of Kawanoue teaches forming a TaN barrier film onto which copper is to be applied, and Miyamoto teaches that a well known way of achieving such a TaN barrier layer is by applying tantalum and then plasma nitriding.

8. Claims 5-6 and 11-12 are rejected under 35 U.S.C. 103(a) as being unpatentable over the admitted state of the prior art in view of Kawanoue as applied to claims 1, 2, 4, 7-9, 13, 14 and 16-21 above, and further in view of Wang et al "Electroless Plating of Copper on Metal-Nitride Diffusion Barriers Initiated by Displacement Plating" (Hereinafter Wang Electroless Article).

The admitted state of the prior art in view of Kawanoue teaches all the features of these claims except the acid system used for the removal of oxide (claim 5, 11) and the reducing agent for the electroless plating (claim 6, 12). The admitted state of the prior art, page 3, lines 10-15, teaches to remove the surface of the barrier film by etching.



However, Wang Electroless Article teaches a method of forming interconnects, where tantalum nitride is used as a barrier material. Page C38. The tantalum nitride is applied to the surface by a process such as sputtering. Page C38, column 2. Then the substrate with TaN is etched with HF: HNO<sub>3</sub>:H<sub>2</sub>O solution (hydrofluoric acid: nitric acid: and water – a diluent of hydrofluoric acid). Page C38, column 2 (the use of the water would also provide that diluted hydrofluoric acid is present). This removes the oxide from the surface. Pages C38-C39 (see paragraph bridging pages). Then electroless copper plating is performed. Page C38, column 2. Moreover, Wang Electroless Article teaches that the reducing agent used for the electroless copper plating bath can be glyoxylic acid. Page C38, column 2.

It would have been obvious to one of ordinary skill in the art at the time the invention was made to modify the admitted state of the prior art in view of Kawanoue to etch treat the tantalum nitride film by immersing in a solution of hydrofluoric acid, nitric acid, and a diluent of hydrofluoric acid to remove oxide as suggested by Wang Electroless Article in order to provide a desirable barrier film, because the admitted state of the prior art in view of Kawanoue teaches forming a TaN barrier film onto which copper is to be applied and etching before copper plating, and Wang Electroless Article teaches that a well known way of achieving such etching for a TaN barrier layer before copper plating is by applying solution treating, which would suggest immersion to apply the solution, with solution of hydrofluoric acid, nitric acid and a diluent of hydrofluoric acid to remove oxide. Thus, for example, a mixture of hydrofluoric acid

and nitric acid would be used. It would further have been obvious to modify the admitted state of the prior art in view of Kawanoue to use glyoxylic acid as the reducing agent for the copper electroless plating bath as suggested by Wang Electroless Article in order to provide a desirable copper plating, because the admitted state of the prior art in view of Kawanoue teaches forming a TaN barrier film onto which copper is applied by electroless plating, and Wang Electroless Article teaches that a well known way of achieving such electroless plating on a TaN barrier film is by using glyoxylic acid as the reducing agent for the electroless plating bath.

### *Response to Arguments*

9. Applicant's arguments filed September 16, 2008 have been fully considered but they are not persuasive.

Applicant argues that in conventional electroless plating process problems of plating a device in a via hole presents a problem as the device size becomes smaller and smaller, and this may result in a void during plating, and that they have found that a native oxide film formed on the barrier layer is the cause of this problem, which they have solved by controlling the thickness of the oxide film, by controlling the N/Ta ratio of the barrier layer. Applicant argues that while Kawanoue teaches a barrier layer with 0.87 N/Ta ratio, for example, this is used in a damascene process using electroplating, where the film layer 20 of TaN and Cu film 17 (seed layer for electroplating) are successively formed by a sputter method, and therefore provides that the TaN layer is

covered by the Cu layer without exposing the TaN layer to the atmosphere, and therefore has no problem with native oxide formation on the TaN layer, while applicant requires this exposure before the electroless plating of Cu. Thus, in the Kawanoue process, a native oxide layer is not formed, and there is no teaching or suggestion about the relation between N/Ta ratio and the thickness of the native oxide layer formed on it, or controlling the thickness of the native oxide by controlling the N/Ta ratio.

The Examiner has reviewed these arguments, however, the rejection above is maintained. While Kawanoue does not indicate to use a barrier coating of the claimed N/Ta ratio for the specific purpose of solving the problem of voids during electroless plating, this is not required for a proper 35 USC 103 rejection. What is required is a motivation to combine the cited references to provide the claimed invention. Here, the primary reference, the admitted state of the prior art, teaches the electroless plating of copper and use of a barrier layer of N and Ta between a surface and the copper layer in interconnections and the exposure of this barrier film to atmosphere followed by removing of the oxide film, as discussed in the rejection below. What the primary reference does not provide is the use of the barrier layer of the claimed N/Ta ratio. The Examiner has cited Kawanoue as providing the teaching and suggestion of using an N/Ta ratio in the claimed range when providing a layer of N and Ta as a barrier layer between a surface and copper in interconnections. The motivation would be the Kawanoue provides that a ratio in the claimed range provides good barrier features as discussed in the reference (note column 9, line 50 through column 10, line 45, discussing

various combinations of features that would be desirable and how to achieve them using a controlled N/Ta ratio). While Kawanoue does not describe electroless plating the overlayer of copper (rather applies it by sputtering), the benefits described by Kawanoue due to the N/Ta ratio are not due to the application method of applying copper but are based on how the interaction between the copper that has been applied and the barrier layer and surface occur. This would occur however the copper is applied. Therefore, one of ordinary skill in the art applying a barrier layer of N and Ta to be used between a surface and a copper layer, such as by the admitted state of the prior art, would find that the composition of the barrier layer would be desirably as that suggested by Kawanoue. While applicant has apparently also discovered that beneficial results occur with the oxide layer thickness when using such compositions in an electroless plating process, this would simply be a matter of discovering latent properties or additional advantages in the prior art, which does not render obvious an otherwise known invention. See MPEP 2145 (II):

Mere recognition of latent properties in the prior art does not render nonobvious an otherwise known invention. In *re Wiseman*, 596 F.2d 1019, 201 USPQ 658 (CCPA 1979) (Claims were directed to grooved carbon disc brakes wherein the grooves were provided to vent steam or vapor during a braking action. A prior art reference taught noncarbon disc brakes which were grooved for the purpose of cooling the faces of the braking members and eliminating dust. The court held the prior art references when combined would overcome the problems of dust and overheating solved by the prior art and would inherently overcome the steam or vapor cause of the problem relied upon for patentability by applicants. Granting a patent on the discovery of an unknown but inherent function (here venting steam or vapor) "would re-move from the public that which is in the public domain by virtue of its inclusion in, or

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obviousness from, the prior art.” 596 F.2d at 1022, 201 USPQ at 661.); In re Baxter Travenol Labs., 952 F.2d 388, 21 USPQ2d 1281 (Fed. Cir. 1991) (Appellant argued that the presence of DEHP as the plasticizer in a blood collection bag unexpectedly suppressed hemolysis and therefore rebutted any prima facie showing of obviousness, however the closest prior art utilizing a DEHP plasticized blood collection bag inherently achieved same result, although this fact was unknown in the prior art.).

“The fact that appellant has recognized another advantage which would flow naturally from following the suggestion of the prior art cannot be the basis for patentability when the differences would otherwise be obvious.” Ex parte Obiaya, 227 USPQ 58, 60 (Bd. Pat. App. & Inter. 1985) (The prior art taught combustion fluid analyzers which used labyrinth heaters to maintain the samples at a uniform temperature. Although appellant showed an unexpectedly shorter response time was obtained when a labyrinth heater was employed, the Board held this advantage would flow naturally from following the suggestion of the prior art.). See also Lantech Inc. v. Kaufman Co. of Ohio Inc., 878 F.2d 1446, 12 USPQ2d 1076, 1077 (Fed. Cir. 1989), cert. denied, 493 U.S. 1058 (1990) (unpublished — not citable as precedent) (“The recitation of an additional advantage associated with doing what the prior art suggests does not lend patentability to an otherwise unpatentable invention.”).

Here, the benefits applicant discusses follow a similar pattern to the case law discussed above.

### *Conclusion*

Any inquiry concerning this communication or earlier communications from the examiner should be directed to Katherine A. Bareford whose telephone number is (571) 272-1413. The examiner can normally be reached on M-F(6:00-3:30) First Friday Off.

If attempts to reach the examiner by telephone are unsuccessful, the examiner’s supervisor, Timothy H. Meeks can be reached on (571) 272-1423. The fax phone number for the organization where this application or proceeding is assigned is 571-273-8300.

Information regarding the status of an application may be obtained from the Patent Application Information Retrieval (PAIR) system. Status information for published applications may be obtained from either Private PAIR or Public PAIR. Status information for unpublished applications is available through Private PAIR only. For more information about the PAIR system, see <http://pair-direct.uspto.gov>. Should you have questions on access to the Private PAIR system, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free). If you would like assistance from a USPTO Customer Service Representative or access to the automated information system, call 800-786-9199 (IN USA OR CANADA) or 571-272-1000.

/Katherine A. Bareford/  
Primary Examiner, Art Unit 1792